

WHAT IS CLAIMED IS:

1. A biofuel cell for generating electricity comprising:

a fuel fluid;

an electron mediator;

a cathode capable of reducing an oxidant in the presence of electrons to form

5 water; and

a bioanode which comprises

(a) an electron conductor;

(b) at least one enzyme capable of reacting with an oxidized form of the
10 electron mediator and the fuel fluid to produce an oxidized form of the fuel fluid and
a reduced form of the electron mediator;

(c) an enzyme immobilization material capable of immobilizing and stabilizing
the enzyme, the material being permeable to the fuel fluid and the electron mediator;
and

15 (d) an electrocatalyst adjacent the electron conductor, an oxidized form of the
electrocatalyst being capable of reacting with the reduced form of the electron
mediator to produce an oxidized form of the electron mediator and a reduced form of
the electrocatalyst, the reduced form of the electrocatalyst being capable of
releasing electrons to the electron conductor.

2. A biofuel cell for generating electricity comprising:

a fuel fluid;

a cathode capable of reducing an oxidant in the presence of electrons to form
5 water; and

a bioanode which comprises

(a) an electron conductor;

(b) at least one enzyme capable of reacting with an oxidized form of an electron mediator and the fuel fluid to produce an oxidized form of the fuel fluid and a reduced form of the electron mediator;

10 (c) an enzyme immobilization material comprising the electron mediator, the enzyme immobilization material being capable of immobilizing and stabilizing the enzyme, the material being permeable to the fuel fluid; and

(d) an electrocatalyst adjacent the electron conductor, an oxidized form of the electrocatalyst being capable of reacting with the reduced form of the electron mediator to produce an oxidized form of the electron mediator and a reduced form of the electrocatalyst, the reduced form of the electrocatalyst being capable of releasing electrons to the electron conductor.

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3. The biofuel cell of claim 1 wherein the enzyme immobilization material comprises a micellar or inverted micellar structure, the material being permeable to the fuel fluid and the electron mediator.

4. The biofuel cell of claim 2 wherein the enzyme immobilization material comprises a micellar or inverted micellar structure, the material being permeable to the fuel fluid.

5. A biofuel cell for generating electricity comprising:

a fuel fluid;

an electron mediator;

a cathode capable of reducing an oxidant in the presence of electrons to form water; and

5 a bioanode for oxidizing the fuel fluid to generate electricity, the bioanode comprising

10 (a) an electron conductor;
(b) at least one enzyme capable of reacting with an oxidized form of the electron mediator and the fuel fluid to produce an oxidized form of the fuel fluid and a reduced form of the electron mediator, the reduced form of the electron mediator being capable of releasing electrons to the electron conductor; and
(c) an enzyme immobilization material capable of immobilizing and stabilizing the enzyme, the material being permeable to the fuel fluid and the electron mediator.

6. A biofuel cell for generating electricity comprising:
a fuel fluid;
a cathode capable of reducing an oxidant in the presence of electrons to form water; and
5 a bioanode for oxidizing the fuel fluid to generate electricity, the bioanode comprising
(a) an electron conductor;
(b) at least one enzyme capable of reacting with an oxidized form of an electron mediator and the fuel fluid to produce an oxidized form of the fuel fluid and a reduced form of the electron mediator, the reduced form of the electron mediator being capable of releasing electrons to the electron conductor; and
10 (c) an enzyme immobilization material comprising the electron mediator, the enzyme immobilization material being capable of immobilizing and stabilizing the enzyme, the material being permeable to the fuel fluid.

7. The biofuel cell of claim 5 wherein the enzyme immobilization material comprises a micellar or inverted micellar structure, the material being permeable to the fuel fluid and the electron mediator.

8. The biofuel cell of claim 6 wherein the enzyme immobilization material comprises a micellar or inverted micellar structure, the material being permeable to the fuel fluid.

9. The biofuel cell of claim 5 wherein the enzyme immobilization material comprises a modified perfluoro sulfonic acid-PTFE copolymer, the material being permeable to the fuel fluid and the electron mediator.

10. The biofuel cell of claim 6 wherein the enzyme immobilization material comprises an alkylammonium salt extracted perfluoro sulfonic acid-PTFE copolymer, the material being permeable to the fuel fluid.

11. The biofuel cell of claim 1 wherein the enzyme immobilization material comprises a modified perfluoro sulfonic acid-PTFE copolymer, the material being permeable to the fuel fluid and the electron mediator.

12. The biofuel cell of claim 2 wherein the enzyme immobilization material comprises a modified perfluoro sulfonic acid-PTFE copolymer, the material being permeable to the fuel fluid.

13. The biofuel cell of claim 2 wherein the electron conductor comprises a carbon-based material, a metallic conductor, a semiconductor, a metal oxide or a modified conductor.

14. The biofuel cell of claim 2 wherein the electron conductor comprises carbon cloth, carbon paper, carbon screen printed electrodes, carbon black, carbon powder, carbon fiber, single-walled carbon nanotubes, double-walled carbon

5 nanotubes, multi-walled carbon nanotubes, carbon nanotube arrays, diamond-coated conductors, glass carbon, mesoporous carbon, graphite, uncompressed graphite worms, delaminated purified flake graphite, high performance graphite, highly ordered pyrolytic graphite, pyrolytic graphite, polycrystalline graphite, gold, platinum, iron, nickel, copper, silver, stainless steel, mercury, tungsten, nanoparticles made of cobalt or diamond, silver-plated nickel screen printed electrodes, metal oxides, metal sulfides, nanoporous titanium oxide, tin oxide coated glass, cerium oxide particles, molybdenum sulfide, boron nitride nanotubes, aerogels modified with carbon, solgels modified with carbon, ruthenium carbon aerogels and mesoporous silicas modified with carbon; silicon or germanium, which can be doped with phosphorus, boron, gallium, arsenic, indium or antimony.

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15. The biofuel cell of claim 13 wherein the electron conductor comprises a carbon-based material.

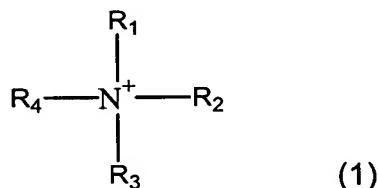
16. The biofuel cell of claim 15 wherein the electron conductor comprises carbon cloth, carbon paper, carbon screen printed electrodes, carbon black, carbon powder, carbon fiber, single-walled carbon nanotubes, double-walled carbon nanotubes, multi-walled carbon nanotubes, carbon nanotube arrays, diamond-coated conductors, glass carbon, mesoporous carbon, graphite, uncompressed graphite worms, delaminated purified flake graphite, high performance graphite, highly ordered pyrolytic graphite, pyrolytic graphite or polycrystalline graphite.

5 17. The biofuel cell of claim 2 wherein the enzyme immobilization material is modified with a hydrophobic cation larger than NH_4^+ .

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18. The biofuel cell of claim 17 wherein the hydrophobic cation comprises an ammonium-based cation, quaternary ammonium cation, alkyltrimethylammonium cation, organic cation, phosphonium cation, triphenylphosphonium, pyridinium cation, imidazolium cation, hexdecylpyridinium, ethidium, viologen, methyl viologen, benzyl viologen, bis(triphenylphosphine)iminium, metal complex, bipridyl metal complex, phenanthroline-based metal complex, $[\text{Ru}(\text{bipyridine})_3]^{2+}$ or $[\text{Fe}(\text{phenanthroline})_3]^{3+}$.

19. The biofuel cell of claim 17 wherein the hydrophobic cation comprises a quaternary ammonium cation represented by formula 1



5 wherein R_1 , R_2 , R_3 and R_4 are independently hydrogen, hydrocarbyl, substituted hydrocarbyl or heterocyclo wherein at least one of R_1 , R_2 , R_3 and R_4 is other than hydrogen.

20. The biofuel cell of claim 19 wherein R_1 , R_2 , R_3 and R_4 are independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl wherein at least one of R_1 , R_2 , R_3 and R_4 is other than hydrogen.

21. The biofuel cell of claim 19 wherein R_1 , R_2 , R_3 and R_4 are the same and are methyl, ethyl, propyl, butyl, pentyl or hexyl.

22. The biofuel cell of claim 19 wherein R_1 , R_2 , R_3 and R_4 are butyl.

23. The biofuel cell of claim 2 wherein the enzyme comprises an oxidoreductase.

24. The biofuel cell of claim 2 wherein the enzyme comprises a dehydrogenase.

25. The biofuel cell of claim 2 wherein the enzyme comprises an alcohol dehydrogenase, aldehyde dehydrogenase, formate dehydrogenase, formaldehyde dehydrogenase, glucose dehydrogenase, glucose oxidase, lactic dehydrogenase, lactose dehydrogenase or pyruvate dehydrogenase.

26. The biofuel cell of claim 25 wherein the enzyme comprises an alcohol dehydrogenase.

27. The biofuel cell of claim 2 wherein the bioanode and the cathode are separated by a salt bridge or a polymer electrolyte membrane.

28. The biofuel cell of claim 27 wherein the bioanode and the cathode are separated by a polymer electrolyte membrane wherein the bioanode, polymer electrolyte membrane and cathode are fabricated into a membrane electrode assembly.

29. The biofuel cell of claim 28 wherein the polymer electrolyte membrane comprises a perfluoro sulfonic acid-polytetrafluoro ethylene (PTFE) copolymer.

30. The biofuel cell of claim 2 further comprising a solution of a fuel fluid.

31. The biofuel cell of claim 30 wherein the fuel fluid comprises ammonia, methanol, ethanol, propanol, isobutanol, butanol and isopropanol, allyl alcohols, aryl alcohols, glycerol, propanediol, mannitol, glucuronate, aldehyde, carbohydrates, glucose, glucose-1, D-glucose, L-glucose, glucose-6-phosphate, lactate, lactate-6-phosphate, D-lactate, L-lactate, fructose, galactose-1, galactose, aldose, sorbose, mannose, glycerate, coenzyme A, acetyl Co-A, malate, isocitrate, formaldehyde, acetaldehyde, acetate, citrate, L-gluconate, beta-hydroxysteroid, alpha-hydroxysteroid, lactaldehyde, testosterone, gluconate, fatty acids, lipids, phosphoglycerate, retinal, estradiol, cyclopentanol, hexadecanol, long-chain alcohols, coniferyl-alcohol, cinnamyl-alcohol, formate, long-chain aldehydes, pyruvate, butanal, acyl-CoA, steroids, amino acids, flavin, NADH, NADH₂, NADPH, NADPH₂ or hydrogen.

32. The biofuel cell of claim 31 wherein the fuel fluid comprises methanol, ethanol or propanol.

33. The biofuel cell of claim 32 wherein the fuel fluid comprises ethanol.

34. The biofuel cell of claim 2 wherein the electron mediator is in solution.

35. The biofuel cell of claim 2 wherein the cathode comprises a biocathode.

36. The biofuel cell of claim 2 wherein the electron conductor comprises an uncompressed graphite worm treated with the electrocatalyst for the electron mediator.

37. The biofuel cell of claim 36 wherein the electrocatalyst for the electron mediator comprises methylene green.

38. The biofuel cell of claim 2 wherein the electrocatalyst for the electron mediator comprises an azine, a conducting polymer or an electroactive polymer.

39. The biofuel cell of claim 2 wherein the electrocatalyst for the electron mediator comprises methylene green, methylene blue, luminol, nitro-fluorenone derivatives, azines, osmium phenanthrolinedione, catechol-pendant terpyridine, toluene blue, cresyl blue, nile blue, neutral red, phenazine derivatives, tioin, azure A, azure B, toluidine blue O, acetophenone, metallophthalocyanines, nile blue A, modified transition metal ligands, 1,10-phenanthroline-5,6-dione, 1,10-phenanthroline-5,6-diol, [Re(phen-dione)(CO)₃Cl], [Re(phen-dione)₃](PF₆)₂, poly(metallophthalocyanine), poly(thionine), quinones, diimines, diaminobenzenes, diaminopyridines, phenothiazine, phenoxyazine, toluidine blue, brilliant cresyl blue, 3,4-dihydroxybenzaldehyde, poly(acrylic acid), poly(azure I), poly(nile blue A), poly(methylene green), poly(methylene blue), polyaniline, polypyridine, polypyrole, polythiophene, poly(thieno[3,4-*b*]thiophene), poly(3-hexylthiophene), poly(3,4-ethylenedioxypyrrole), poly(isothianaphthene), poly(3,4-ethylenedioxothiophene), poly(difluoroacetylene), poly(4-dicyanomethylene-4H-cyclopenta[2,1-*b*;3,4-*b*]dithiophene), poly(3-(4-fluorophenyl)thiophene) or poly(neutral red).

40. The biofuel cell of claim 2 wherein the electrocatalyst for the electron mediator comprises methylene green.

41. The biofuel cell of claim 2 wherein the electrocatalyst for the electron mediator comprises poly(methylene green).

42. The biofuel cell of claim 2 wherein the enzyme immobilization material comprises perfluoro sulfonic acid-polytetrafluoro ethylene (PTFE) copolymer, modified perfluoro sulfonic acid-polytetrafluoro ethylene (PTFE) copolymer, polysulfone, micellar polymers, poly(ethylene oxide) based block copolymers, polymers formed from microemulsion, polymers formed from micellar polymerization, copolymers of alkyl methacrylates, alkyl acrylates and styrenes, ceramics, sodium bis(2-ethylhexyl)sulfosuccinate, sodium dioctylsulfosuccinate, lipids, phospholipids, sodium dodecyl sulfate, decyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, (4-[(2-hydroxyl-1-
10 naphthalenyl)azo]benzenesulfonic acid monosodium salt), linoleic acids, linolenic acids, colloids, liposomes or micelle networks.

43. The biofuel cell of claim 42 wherein the enzyme immobilization material comprises a perfluoro sulfonic acid-polytetrafluoro ethylene (PTFE) copolymer.

44. The biofuel cell of claim 42 wherein the enzyme immobilization material comprises a modified perfluoro sulfonic acid-polytetrafluoro ethylene (PTFE) copolymer.

45. The biofuel cell of claim 2 wherein the electron mediator comprises nicotinamide adenine dinucleotide (NAD), flavin adenine dinucleotide (FAD) or nicotinamide adenine dinucleotide phosphate (NADP).

46. The biofuel cell of claim 2 wherein the electron mediator comprises pyrroloquinoline quinone, phenazine methosulfate, dichlorophenol indophenol, short chain ubiquinones or potassium ferricyanide.

47. The biofuel cell of claim 12 wherein the electron conductor comprises an uncompressed graphite worm treated with poly(methylene green), the modified perfluoro sulfonic acid-PTFE copolymer is modified with a tetrabutylammonium ion, the enzyme comprises an alcohol dehydrogenase and further comprises a solution containing ethanol and NAD⁺.

5 48. A method of generating electricity using the biofuel cell of claim 2 comprising

 (a) oxidizing the fuel fluid at the bioanode and reducing the oxidant at the cathode;

5 (b) reducing the oxidized form of the electron mediator during the oxidization of the fuel fluid at the bioanode;

 (c) reducing the electrocatalyst; and

 (d) oxidizing the electrocatalyst at the electron conductor.

49. A method of generating electricity using the biofuel cell of claim 6 comprising

 (a) oxidizing the fuel fluid at the bioanode and reducing the oxidant at the cathode;

5 (b) reducing the oxidized form of the electron mediator during the oxidization of the fuel fluid at the bioanode; and

 (c) oxidizing the electron mediator at the electron conductor.

50. The method of claim 48 wherein the fuel fluid comprises ammonia, methanol, ethanol, propanol, isobutanol, butanol and isopropanol, allyl alcohols, aryl alcohols, glycerol, propanediol, mannitol, glucuronate, aldehyde, carbohydrates,

5 glucose, glucose-1, D-glucose, L-glucose, glucose-6-phosphate, lactate, lactate-6-phosphate, D-lactate, L-lactate, fructose, galactose-1, galactose, aldose, sorbose, mannose, glycerate, coenzyme A, acetyl Co-A, malate, isocitrate, formaldehyde, acetaldehyde, acetate, citrate, L-gluconate, beta-hydroxysteroid, alpha-hydroxysteroid, lactaldehyde, testosterone, gluconate, fatty acids, lipids, phosphoglycerate, retinal, estradiol, cyclopentanol, hexadecanol, long-chain alcohols, coniferyl-alcohol, cinnamyl-alcohol, formate, long-chain aldehydes, pyruvate, butanal, acyl-CoA, steroids, amino acids, flavin, NADH, NADH₂, NADPH, NADPH₂ or hydrogen.

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51. The method of claim 48 wherein the fuel fluid comprises methanol, ethanol or propanol.

52. The method of claim 50 wherein the fuel fluid comprises ethanol.

53. The method of claim 48 wherein the electrocatalyst for an electron mediator comprises an azine, a conducting polymer or an electroactive polymer.

54. The method of claim 48 wherein the electrocatalyst for the electron mediator comprises methylene green, methylene blue, luminol, nitro-fluorenone derivatives, azines, osmium phenanthrolinedione, catechol-pendant terpyridine, toluene blue, cresyl blue, nile blue, neutral red, phenazine derivatives, tioin, azure A, azure B, toluidine blue O, acetophenone, metallophthalocyanines, nile blue A, modified transition metal ligands, 1,10-phenanthroline-5,6-dione, 1,10-phenanthroline-5,6-diol, [Re(phen-dione)(CO)₃Cl], [Re(phen-dione)₃](PF₆)₂, poly(metallophthalocyanine), poly(thionine), quinones, diimines, diaminobenzenes, diaminopyridines, phenothiazine, phenoxazine, toluidine blue, brilliant cresyl blue,

10 3,4-dihydroxybenzaldehyde, poly(acrylic acid), poly(azure I), poly(nile blue A),
poly(methylene green), poly(methylene blue), polyaniline, polypyridine, polypyrole,
polythiophene, poly(thieno[3,4-*b*]thiophene), poly(3-hexylthiophene), poly(3,4-
ethylenedioxypyrrole), poly(isothianaphthene), poly(3,4-ethylenedioxothiophene),
poly(difluoroacetylene), poly(4-dicyanomethylene-4H-cyclopenta[2,1-*b*;3,4-
-*b*]dithiophene), poly(3-(4-fluorophenyl)thiophene) or poly(neutral red).

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55. The method of claim 54 wherein the electrocatalyst for the electron mediator comprises methylene green.

56. The method of claim 54 wherein the electrocatalyst for the electron mediator comprises poly(methylene green).

57. The method of claim 48 wherein the electron mediator comprises nicotinamide adenine dinucleotide (NAD), flavin adenine dinucleotide (FAD) or nicotinamide adenine dinucleotide phosphate (NADP).

58. The method of claim 57 wherein the electron mediator comprises NAD⁺.

59. The method of claim 48 wherein the electron conductor comprises an uncompressed graphite worm treated with poly(methylene green), the modified perfluoro sulfonic acid-PTFE copolymer is modified with a tetrabutylammonium ion, the enzyme comprises an alcohol dehydrogenase, the fuel fluid comprises ethanol and the electron mediator comprises NAD⁺.

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60. The method of claim 49 wherein the electron mediator comprises pyrroloquinoline quinone, phenazine methosulfate, dichlorophenol indophenol, short chain ubiquinones or potassium ferricyanide.

61. The method of claim 60 wherein the electron mediator comprises pyrroloquinoline quinone (PQQ).

62. The method of claim 49 wherein the electron conductor comprises carbon cloth, the modified perfluoro sulfonic acid-PTFE copolymer is modified with a tetrabutylammonium ion, the enzyme comprises an alcohol dehydrogenase, the fuel fluid comprises ethanol and the electron mediator comprises PQQ.

63. An enzyme immobilized in a non-naturally occurring colloidal immobilization material capable of immobilizing and stabilizing the enzyme, the material being permeable to a compound smaller than the enzyme.

64. An enzyme immobilized in an acellular, colloidal immobilization material capable of immobilizing and stabilizing the enzyme, the material being permeable to a compound smaller than the enzyme.

65. An enzyme immobilized in a micellar or inverted micellar immobilization material capable of immobilizing and stabilizing the enzyme, the material being permeable to a compound smaller than the enzyme.

66. An enzyme immobilized in a cation-modified perfluoro sulfonic acid-PTFE copolymer capable of immobilizing and stabilizing the enzyme, the material being permeable to a compound smaller than the enzyme.

67. The immobilized enzyme of claim 65 wherein the enzyme comprises an alcohol dehydrogenase, aldehyde dehydrogenase, formate dehydrogenase, formaldehyde dehydrogenase, glucose dehydrogenase, glucose oxidase, lactic dehydrogenase, lactose dehydrogenase or pyruvate dehydrogenase.

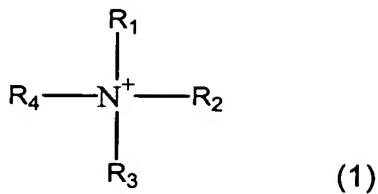
68. The immobilized enzyme of claim 65 wherein the enzyme is active for at least about 30, 60, 90, 120, 150, 180, 240, 300 or 365 days.

69. The immobilized enzyme of claim 65 wherein the immobilization material comprises a cation modified perfluoro sulfonic acid-PTFE copolymer.

70. The immobilized enzyme of claim 69 wherein the cation modified perfluoro sulfonic acid-PTFE copolymer is modified with a hydrophobic cation larger than NH_4^+ .

71. The immobilized enzyme of claim 70 wherein the hydrophobic cation comprises an ammonium-based cation, quaternary ammonium cation, alkyltrimethylammonium cation, organic cation, phosphonium cation, triphenylphosphonium, pyridinium cation, imidazolium cation, hexadecylpyridinium, ethidium, viologen, methyl viologen and benzyl viologen, bis(triphenylphosphine)iminium, metal complex, bipridyl metal complex, phenanthroline-based metal complex, $[\text{Ru}(\text{bipyridine})_3]^{2+}$ or $[\text{Fe}(\text{phenanthroline})_3]^{3+}$.

72. The immobilized enzyme of claim 70 wherein the hydrophobic cation comprises a quaternary ammonium cation represented by formula 1



5 wherein R_1 , R_2 , R_3 and R_4 are independently hydrogen, hydrocarbyl, substituted hydrocarbyl or heterocyclo wherein at least one of R_1 , R_2 , R_3 and R_4 is other than hydrogen.

73. The immobilized enzyme of claim 72 wherein R_1 , R_2 , R_3 and R_4 are independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl wherein at least one of R_1 , R_2 , R_3 and R_4 is other than hydrogen.

74. The immobilized enzyme of claim 72 wherein R_1 , R_2 , R_3 and R_4 are the same and are methyl, ethyl, propyl, butyl, pentyl or hexyl.

75. The immobilized enzyme of claim 72 wherein R_1 , R_2 , R_3 and R_4 are butyl.

76. The immobilized enzyme of claim 65 wherein the compounds smaller than the enzymes comprise ammonia, methanol, ethanol, propanol, isobutanol, butanol and isopropanol, allyl alcohols, aryl alcohols, glycerol, propanediol, mannitol, glucuronate, aldehyde, carbohydrates, glucose, glucose-1, D-glucose, L-glucose, glucose-6-phosphate, lactate, lactate-6-phosphate, D-lactate, L-lactate, fructose, galactose-1, galactose, aldose, sorbose, mannose, glycerate, coenzyme A, acetyl Co-A, malate, isocitrate, formaldehyde, acetaldehyde, acetate, citrate, L-gluconate, beta-hydroxysteroid, alpha-hydroxysteroid, lactaldehyde, testosterone, gluconate,

10 fatty acids, lipids, phosphoglycerate, retinal, estradiol, cyclopentanol, hexadecanol, long-chain alcohols, coniferyl-alcohol, cinnamyl-alcohol, formate, long-chain aldehydes, pyruvate, butanal, acyl-CoA, steroids, amino acids, flavin, NADH, NADH₂, NADPH, NADPH₂ or hydrogen.

77. Use of the immobilized enzyme of claim 65 in a biofuel cell, a biosensor, a bioprocessor, a bioassay, an enzyme sensor, a bioreactor, enzyme therapy, an immunoassay or a biomimic.

78. A fuel cell comprising a bioanode and a cathode, wherein (a) the bioanode comprises a redox polymer film, a modified ion exchange polymer membrane and a dehydrogenase, and (b) the dehydrogenase is incorporated within a micellar compartment of the modified ion exchange polymer membrane.

79. The fuel cell of claim 78 wherein the modified ion exchange polymer membrane is a salt-extracted quaternary ammonium treated perfluorinated ion exchange polymer.

80. The fuel cell of claim 79 wherein the perfluorinated ion exchange polymer is a Nafion® polymer.

81. The fuel cell of claim 80 wherein the quaternary ammonium is tetrabutylammonium bromide.

82. The fuel cell of claim 78 wherein the redox polymer film is polymethylene green.

83. The fuel cell of claim 78 wherein the dehydrogenase is an alcohol dehydrogenase.

84. The fuel cell of claim 83 further comprising an aldehyde dehydrogenase.

85. The fuel cell of claim 78 wherein the cathode is a biocathode, which comprises a second redox polymer film, a second modified ion exchange polymer membrane and an O₂-reductase.

86. The fuel cell of claim 85 wherein the second modified ion exchange polymer membrane is a salt-extracted quaternary ammonium treated Nafion® polymer, the second redox polymer film is a poly(N-vinyl-imidiazole), and the O₂-reductase is a laccase.

87. A biofuel cell comprising a bioanode and a cathode, wherein (a) the bioanode comprises a carbon cloth, a redox polymer film of polymethylene green, a salt-extracted tetrabutylammonium bromide-treated perfluorinated ion exchange polymer, and an alcohol dehydrogenase, (b) the alcohol dehydrogenase is incorporated within a micellar compartment of the salt-extracted tetrabutylammonium bromide treated perfluorinated ion exchange polymer, and (c) the redox polymer film of polymethylene green lies in apposition to the salt-extracted tetrabutylammonium bromide-treated perfluorinated ion exchange polymer and the carbon cloth.

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88. The biofuel cell of claim 87 wherein the salt-extracted tetrabutylammonium bromide treated perfluorinated ion exchange polymer is a salt-extracted tetrabutylammonium bromide treated Nafion® polymer.

89. The biofuel cell of claim 88 further comprising an aldehyde dehydrogenase, wherein the aldehyde dehydrogenase is incorporated within a micellar compartment of the salt-extracted tetrabutylammonium bromide treated perfluorinated ion exchange polymer.

90. A bioanode comprising a support membrane, redox polymer, quaternary ammonium salt-modified perfluorinated ion exchange polymer and a dehydrogenase, wherein (a) the dehydrogenase is incorporated within the quaternary ammonium salt-modified perfluorinated ion exchange polymer, and (b) the redox polymer is juxtaposed with the support membrane and the quaternary ammonium salt-modified perfluorinated ion exchange polymer.

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91. The bioanode of claim 90 wherein the redox polymer is a polymethylene green.

92. The bioanode of claim 90 wherein the quaternary ammonium salt-modified perfluorinated ion exchange polymer is a quaternary ammonium salt-modified Nafion® polymer.

93. The bioanode of claim 90 wherein the dehydrogenase is selected from the group consisting of alcohol dehydrogenase, aldehyde dehydrogenase, formaldehyde dehydrogenase, glucose dehydrogenase and formate dehydrogenase.

94. The bioanode of claim 90 wherein the dehydrogenase is an alcohol dehydrogenase.

95. The bioanode of claim 94 further comprising an aldehyde dehydrogenase.

96. The bioanode of claim 90 wherein the support membrane is a carbon cloth.

97. A bioanode comprising a carbon cloth support membrane, a polymethylene green redox polymer, quaternary ammonium salt-modified perfluorinated ion exchange polymer and an alcohol dehydrogenase, wherein (a) the dehydrogenase is incorporated within the quaternary ammonium salt-modified Nafion® polymer, and (b) the redox polymer is juxtaposed with the carbon cloth support membrane and the quaternary ammonium salt-modified Nafion® polymer.

5 98. The bioanode of claim 97 further comprising an aldehyde dehydrogenase incorporated within the quaternary ammonium salt-modified Nafion® polymer.

99. A perfluorinated ion exchange polymer comprising a modification and one or more enzymes, wherein the enzyme is incorporated within a micelle of the modified perfluorinated ion exchange polymer.

100. The perfluorinated ion exchange polymer of claim 99 wherein the perfluorinated ion exchange polymer is a Nafion® polymer.

101. The perfluorinated ion exchange polymer of claim 99 wherein the modification causes a decrease in proton exchange capacity of the polymer relative to an unmodified perfluorinated ion exchange polymer.

102. The perfluorinated ion exchange polymer of claim 99 wherein the enzyme is a redox enzyme that catalyzes the oxidation of an organic fuel and the reduction of a cofactor.

103. The perfluorinated ion exchange polymer of claim 102 wherein the cofactor is selected from the group consisting of NAD⁺, NADP⁺ and FAD.

104. The perfluorinated ion exchange polymer of claim 102 wherein the cofactor is NAD⁺.

105. The perfluorinated ion exchange polymer of claim 102 wherein the enzyme is selected from the group consisting of alcohol dehydrogenase, aldehyde dehydrogenase, glyceraldehyde-3-phosphate dehydrogenase, formaldehyde dehydrogenase, formate dehydrogenase, lactate dehydrogenase, glucose dehydrogenase and pyruvate dehydrogenase.

5 106. The perfluorinated ion exchange polymer of claim 102 wherein the enzyme is an alcohol dehydrogenase or aldehyde dehydrogenase.

107. A method of generating electrical power, comprising oxidizing an organic fuel at an anode in the presence of a redox enzyme, which is incorporated in the anode; and reducing oxygen at a cathode, wherein (a) the anode comprises an ion conducting polymer, a redox polymer membrane and a supporting membrane (a) the redox enzyme is immobilized within the ion conducting polymer, (b) a cofactor is reduced during the oxidization reaction at the anode, (c) a redox polymer membrane catalyzes the oxidation of the reduced cofactor.

5 108. The method of claim 107 wherein the redox polymer membrane comprises a polymethylene green.

109. The method of claim 107 wherein the ion conducting polymer comprises a quaternary ammonium bromide treated Nafion® polymer.

110. The method of claim 107 wherein the cofactor is NAD⁺ and the redox enzyme is an alcohol dehydrognase or aldehyde dehydrogenase.

111. The method of claim 107 wherein the organic fuel is an alcohol.

112. A method of generating electrical power, comprising oxidizing an alcohol at an anode and reducing oxygen at a cathode, wherein (a) the anode comprises a polymethylene green polymer, a quaternary ammonium bromide-treated Nafion®

polymer, a carbon fiber supporting membrane and an alcohol dehydrogenase; (b) 5 the alcohol dehydrogenase is immobilized within a micelle compartment of the quaternary ammonium bromide-treated Nafion® polymer, (c) a NAD⁺ is reduced to NADH during the oxidization of the alcohol at the anode, and (d) the NADH is electro-oxidized to NAD+ at the polymethylene green polymer.